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A green, low-cost, and highly effective strategy to enhance the performance of hybrid solar cells: Post-deposition ligand exchange by acetic acid

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ABSTRACT

We utilize an adsorption/desorption process between the excess acetic acid in solution and the bound oleate ions on the surface of CdSe quantum dots to achieve ligand exchange process in the hybrid film of poly (3-hexylthione) (P3HT): CdSe quantum dots (QDs). By this post-deposition ligand exchange method, we achieved hybrid solar cells with power conversion efficiency of nearly 2% at low annealing temperature (120 °C). Compared to the thiols that are widely used in hybrid solar cells, acetic acid shows its advantages of environmental friendliness, non-toxicity and mild odors. As such, our method is attractive for future hybrid solar cell applications.

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1. Introduction

Solution-processed organic solar cells are receiving much attention recently as a potentially competitive technology for green energy with the advantages of low cost, light weight, and high flexibility on appropriate substrates [1–6]. Attributed to the significant modification in active layer, device structure, and fabrication techniques, power conversion efficiencies (PCEs) over 9% [2] and 7% [4] have been achieved for polymer-based and small molecule-based solar cells, respectively, with the bulk heterojunction (BHJ) architecture. Meanwhile, solution-processed hybrid solar cells (HSCs) using inorganic semiconductor nanocrystals as electron acceptors are emerging as a competitive alternative due to their intrinsic higher electron mobility and enhanced optical absorption compared to organic acceptors, e.g. [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) [7–11]. So far, varied semiconductor nanocrystals, such as CdSe [8,9,11], ZnO [12], CdTe [13], PbS [10], and TiO₂ [14,15], have been used to fabricate HSCs in BHJ structure exhibiting PCE mostly below 4%.

So many efforts such as tuning inorganic nanocrystal size and shape [7,16–20], surface modification of nanocrystals [10,11,21–26],

introducing low band gap conjugated polymers [8,10,27], functionalization of conjugated polymers [13,28], and optimizing device structures [8,13,29] were reported, aiming at improving the performance of HSCs. Among them, the surface modification of inorganic nanocrystals has been considered to be an effective way to enhance the performance of HSCs [9,11,30,31]. The synthesis of nanocrystals can be carried out by pyrolysis of organometallic reagents by injection at high temperature into a coordinating organic ligand solution such as long-chain carboxylic acids, alkylphosphines, and alkylphosphine oxides [32]. Typically these organic ligands contain metal coordinating heading groups, which have a high affinity to the electron deficient metal atoms at the surface of the nanocrystals, and can combine to the nanocrystals firmly, thus inhibiting further growth and aggregation of nanocrystals [32]. These nonconductive surfactants on the surface of as-synthesized nanocrystals have disastrous effects on the coupling among inorganic nanocrystals and between conjugated polymers and inorganic nanocrystals [33–36]. If the nonconductive surfactants are replaced by short-chain ligands, the performance of HSCs could be improved [34–37]. Pyridine is widely used in the solution exchange process which can partly remove the long-chain ligands due to its weak interaction towards nanocrystals [7,23,38]. In order to replace the long-chain ligands more completely, recently a post-deposition ligand exchange protocol using small molecules such as amine [23,39], thiol [10,11,21], and hydrazine [40] has become popular. In the previous work, we have developed a post-deposition treatment using *n*-butanethiol to remove the oleic

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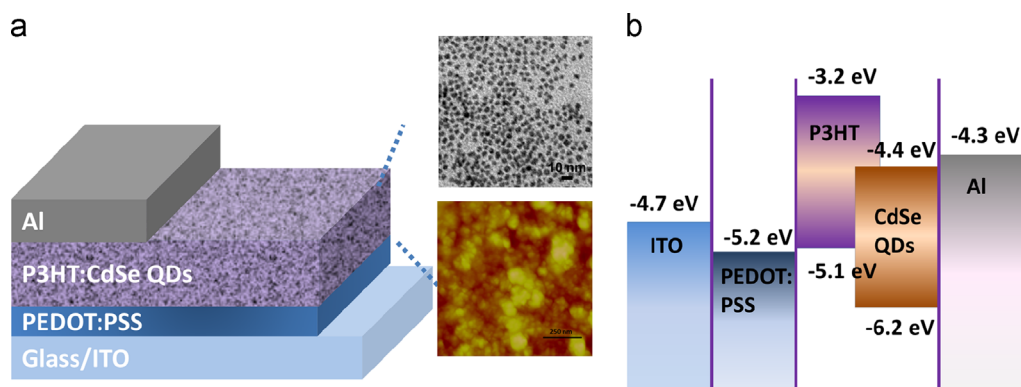


Fig. 1. (a) Schematic of ITO/PEDOT:PSS/P3HT:CdSe QDs/Al device architecture. The right images show TEM image of CdSe QDs and AFM height image of the hybrid films and (b) Energy level diagram of the hybrid solar cells.

acid chains on the surface of nanocrystals so as to enhance the performance of HSCs based on poly (3-hexylthione) (P3HT):CdSe quantum dots (QDs). We achieved a PCE of 3.09%, which is the highest value for HSCs based on P3HT and CdSe QDs so far [11].

Though the thiols are efficient to modify the surface of CdSe nanocrystals to achieve HSCs with high performance, they are toxic, harmful to the environment and have nauseous odors. Instead, safe and environmentally friendly modifiers should be developed to enhance the performance of HSCs. Acids could be a group of molecules with potential application for modification. Fritzinger et al. has demonstrated that the addition of excess oleic acid to a purified oleic acid capped CdSe QDs dispersion can establish an adsorption/desorption equilibrium involving a proton transfer step between excess oleic acid and bound oleate ions [41]. Subsequently, Rosanna et al. reported that the post-deposition treatments with carboxylic acids on films of CdSe@CdTe core-shell tetrapod shaped nanocrystals can replace the long-chain phosphoric acid molecules on the surface of nanocrystals with short-chain carboxylic acid and the efficiency of bilayer solar cells based on the treated nanocrystal films with P3HT layer on top can be improved by 100% to 0.58%, compared to that of the cells based on pyridine treated nanocrystals [42].

Here, for the first time we report that in the P3HT:CdSe QDs hybrid films the oleate ions on the surfaces of CdSe QDs can be replaced by acetic acid, resulting in the enhanced performance of the hybrid solar cells. The achieved PCE is reaching 2%. And the mechanism of the photovoltaic performance improvement is also investigated in this work.

2. Experiments

2.1. CdSe QDs synthesis and hybrid solution preparation

CdSe QDs were synthesized according to the reported procedure [29]. In a typical synthetic process, CdO (76 mg), trioctylphosphine oxide (TOPO, 3.0 g) and oleic acid (OA, 3.0 ml) were added into the reactor and the mixture was heated to 285 °C under vigorous stirring in nitrogen atmosphere. Se (80 mg) was added into trioctylphosphine (TOP, 1.0 ml) and the mixture was sonicated until the solution became clear. Then the Se-TOP solution was quickly injected into the reactor. 5 min later, the hot solution was quickly transferred into toluene (5 ml). The as-prepared CdSe QDs were washed in methanol and centrifuged for two times, and then dispersed in pyridine (15 ml) and stirred for 24 h. The resulting nanocrystals were flocculated by hexane and centrifuged.

P3HT:CdSe QDs blended solution was prepared by dispersing CdSe QDs (30 mg) and dissolving P3HT (Luminescence Technology

Corp., 3.3 mg) in a mixture solvent of chlorobenzene and pyridine ($v:v=9:1$, 1 ml) and stirred overnight.

2.2. Device fabrication

Prior to fabrication, the substrates were cleaned by sonication using detergent, deionized water, acetone, and isopropanol sequentially for every 15 min followed by 15 min of ultraviolet ozone treatment. Then a layer of poly (3, 4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) (Baytron P Al4083) was spin-coated onto the cleaned ITO and baked in air at 140 °C for 15 min. Then the substrates were transferred to a glovebox for spin coating of P3HT:CdSe QDs active layer with the thickness of about 70 nm. For the sample that undergoes ligand exchange, the substrate was dipped in the 0.1 M acetic acid (in acetonitrile) solution for 60 s, followed by a rinse with pure acetonitrile. Then all the samples were annealed at different temperatures for 15 min. Subsequently, samples were loaded into a vacuum deposition chamber (background pressure $\approx 5 \times 10^{-4}$ Pa) to deposit 120 nm thick aluminum cathode with a shadow mask (device area of 9 mm²). Charge carrier mobility in blended films was measured by the space charge limited current (SCLC) method. The hole-only devices with the same active layer thickness as that in PSCs were fabricated with a structure of ITO/PEDOT:PSS/P3HT:CdSe/MoO₃(10 nm)/Al. The electron-only devices were fabricated in a structure of glass/Al/P3HT:CdSe/Al, for which a layer of 120 nm thick Al was first deposited onto the glass substrate and then the P3HT:CdSe QDs solution was spin coated on the Al-covered substrate followed by depositing a layer of 120 nm thick Al. The treatments of the active layer were the same as fabrication of hybrid solar cells and the area for those electron-only and hole-only devices was 9 mm².

2.3. Film and device characterization

The current density–voltage (J – V) curves were measured with Keithley 236 measurement source units at room temperature in air. The photocurrent was measured under a calibrated solar simulator (Abet 300 W) at 100 mW cm⁻², and the light intensity was calibrated with a standard photovoltaic reference cell. External quantum efficiency (EQE) spectrum was measured with Stanford lock-in amplifier 8300 unit. The absorption spectra of the samples on ITO/PEDOT:PSS substrates were recorded on a UV–visible spectrophotometer (UV-2450, Shimadzu Corporation, Japan). The morphological structures of the P3HT:CdSe QDs hybrid films were investigated by a Veeco Multimode atomic force microscopy (AFM) in the tapping mode. The steady-state photoluminescence (PL) spectra were taken on a HORIBA Jobin Yvon FluoroMax-4 spectrofluorometer. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a BRUKER Vector 22 spectrofluorometer. The

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